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(54) Title: SILICONE RESINS AND THEIR PREPARATION

(57) Abstract: A curable silicone resin comprises siloxane units of the formula RR'2Si01/2, where R represents a hydrogen atom or an alkenyl group having 1 to 6 carbon atoms and each R' represents an alkyl group having 1 to 4 carbon atoms or an aryl group, siloxane units of the formula ASi03/2, where A represents an aryl or alkyl group, siloxane units of the formula Si04/2 and optionally siloxane units of the formula HSi03/2. The resin can be cured to a heat resistant silicone resin having a low coefficient of thermal expansion.

SILICONE RESINS AND THEIR PREPARATION

Field of the Invention

[0001] This invention relates to silicone resins curable by addition polymerisation and/or hydrosilylation, to methods of preparation of the curable resins, and also to processes for curing the resins and to cured resins produced thereby.

Background to the Invention

[0002] There is an increasing need for resins with good dimensional stability (low coefficient of thermal expansion (CTE), high glass transition temperature Tg and high modulus) and moisture and heat resistance over a wide temperature range. There is a particular need for resins which can be applied in a curable state and which can be cured in a thick section and are thus suitable for encapsulating delicate substrates, for example as underfill for microelectronic device packaging, as matrix resin in composites, and also in coatings such as wafer level and solar panel coatings, in planarization layers for Flat Panel Displays and in photonic devices.

[0003] Silicone resins have excellent heat resistance and are moisture repellent but typically have a CTE in the range 110 to 300 ppm/°C, compared to 50 to 120 ppm/°C for most organic polymers and resins. The present invention seeks to produce silicone resins having reduce CTE in the cured state so that they are more suitable for the uses listed above

[0004] JP-A-61-225253 describes adding 25% silicone to a novolak-type phenolic resin for the preparation of a thermosetting resin moulding composition. Siloxane particles made of at least 90% silicone resin containing dimethylhydrogensilyl units cured with vinyl- and SiH- functional siloxanes were dispersed into the organic matrix with up to 60% of molten silica filler.

[0005] US-A-6124407 describes a silicone composition comprising (A) 100 parts by weight of a polydiorganosiloxane containing an average of at least two silicon-bonded alkenyl groups per molecule; (B) 75 to 150 parts by weight of an organopolysiloxane resin containing an average of from 2.5 to 7.5 mole percent of alkenyl groups; (C) an organohydrogenpolysiloxane having an average of at least three silicon-bonded hydrogen atoms per molecule in an amount to provide from one to three silicon-bonded hydrogen atoms per alkenyl group in components (A) and (B) combined; (D) an adhesion promoter in an amount to effect adhesion of the composition to a substrate; and (E) a hydrosilylation catalyst in an amount to cure the composition. The composition is useful as an encapsulant in chip scale packages.

[0006] US-A-6310146 describes a cured silsesquioxane resin prepared from a silsesquioxane copolymer, a silyl-terminated hydrocarbon, and a hydrosilylation reaction catalyst. The curing temperature described is 60-260°C.

Summary of the Invention

[0007] According to one aspect of the present invention, a curable silicone resin comprises siloxane M units of the formula $RR'_2SiO_{1/2}$, where R represents a hydrogen atom or an alkenyl group having 1 to 6 carbon atoms and each R' represents an alkyl group having 1 to 4 carbon atoms or an aryl group, siloxane T units of the formula $ArSiO_{3/2}$, where Ar represents an aryl group, siloxane Q units of the formula $SiO_{4/2}$ and optionally siloxane T units of the formula $HSiO_{3/2}$.

[0008] A process according to another aspect of the invention for the preparation of a curable silicone resin comprising siloxane M units of the formula $RR'_2SiO_{1/2}$, where R represents a hydrogen atom or an alkenyl group having 1 to 6 carbon atoms and each R' represents an alkyl group having 1 to 4 carbon atoms or an aryl group, siloxane T units of the formula $ASiO_{3/2}$, where A represents an aryl group or an alkyl group having 1 to 4 carbon atoms, siloxane Q units of the formula $SiO_{4/2}$ and optionally siloxane T units of the formula

$HSiO_{3/2}$, comprises treating a silicone resin comprising siloxane T units of the formula $ASiO_{3/2}$ and $HSiO_{3/2}$ and optionally siloxane M units of the formula $RR'_2SiO_{1/2}$ in solution with a base to condense at least some of the $HSiO_{3/2}$ units to form $SiO_{4/2}$ units, and reacting the resulting resin solution with a chlorosilane of the formula RR'2SiCl.

[0009] The invention also includes a process for the preparation of a cured heat resistant silicone resin having a low coefficient of thermal expansion, characterised in that a curable silicone resin as described above is reacted with a curing agent having at least one functional group reactive with the group R. The presence of $SiO_{4/2}$ units in the curable resin leads to a cured resin of low CTE, increased Tg and modulus and high thermal stability.

Detailed description of the Invention

[0010] The groups R in the siloxane M units $RR'_2SiO_{1/2}$ are preferably alkenyl groups, most preferably vinyl groups although allyl or hexenyl groups are alternatives. The groups R' are most preferably methyl groups but can be other alkyl groups having up to 4 carbon atoms, for example ethyl groups, or aryl groups, particularly phenyl. The groups R' can be the same or different. The siloxane units $RR'_2SiO_{1/2}$ can for example be vinyldimethylsiloxy or vinylmethylphenylsiloxy units.

[0011] The groups R in the siloxane M units $RR'_2SiO_{1/2}$ can alternatively be hydrogen atoms. The siloxane units $RR'_2SiO_{1/2}$ can for example be dimethylhydrogensiloxy or methylphenylhydrogensiloxy units.

[0012] The aryl groups Ar in the siloxane T units of the formula $ArSiO_{3/2}$ are preferably phenyl groups, although naphthyl or tolyl groups are alternatives. The aryl groups enhance the thermal stability of the cured silicone resin. Preferably, at least 5 mol%, most preferably at least 20%, of the siloxane units of the resin are of the formula ArSiO3/2 up to 50 or even 70 mol% $ArSiO_{3/2}$ units. The process of the invention can also be carried out using

T units of the formula $ASiO_{3/2}$, where A represents an alkyl group having 1 to 4 carbon atoms, for example a methyl or ethyl group.

[0013] In a preferred process according to the invention for the preparation of a curable silicone resin, a silicone resin comprising siloxane T units of the formula $ASiO_{3/2}$ and $HSiO_{3/2}$ is treated in solution with a base to condense at least some of the $HSiO_{3/2}$ units to form $SiO_{4/2}$ units, and the resulting resin solution is reacted with a chlorosilane of the formula RR'_2SiCl. The group A is preferably an aryl groups but can alternatively be a 1-4C alkyl group. The starting resin comprising siloxane T units preferably also comprises siloxane M units of the formula $RR'_2SiO_{1/2}$. Such a resin can for example be prepared by reacting trichlorosilane HSiCl3 with a chlorosilane of the formula ASiCl3 and preferably also a chlorosilane of the formula RR'_2SiCl in the presence of water and a dipolar aprotic solvent which is at least partially miscible with water, for example tetrahydrofuran (THF), dioxane or a ketone containing 4 to 7 carbon atoms such as methyl isobutyl ketone (MIBK), methyl ethyl ketone or methyl isoamyl ketone.

[0014] The base which is used to treat the silicone resin is preferably a solution of an alkali metal salt of a weak acid such as a carboxylic acid, for example sodium acetate, sodium hydrogen phosphate or sodium tetraborate. An aqueous and/or organic solvent solution can be used. A preferred solvent mixture comprises water and a dipolar aprotic solvent which is at least partially miscible with water, for example a ketone having 4 to 7 carbon atoms, as described above, or a cyclic ether such as tetrahydrofuran or dioxane. Alternatively the base may comprise an amine, preferably a tertiary amine, particularly a trialkyl amine such as triethylamine or tripropylamine, or alternatively pyridine or dimethylaminopropanol. The base can for example be an aqueous solution of triethylamine. A tertiary amine can act as both base and as a dipolar aprotic solvent, so that one base reagent comprises a solution of an alkali metal salt of a weak acid in a solvent mixture of water and a tertiary amine. The base treatment causes hydrolysis of some of the Si-H groups of the resin to Si-OH groups and subsequent condensation of the Si-OH groups to Si-O-Si linkages, thus converting at least some of the $HSiO_{3/2}$ units to form $SiO_{4/2}$ units.

[0015] The degree of conversion of HSiO3/2 units to SiO4/2 units can be controlled by controlling the strength and concentration of the base used to treat the resin, the time of contact between the resin and the base and the temperature of the reaction. The base strength and concentration and time and temperature of treatment are preferably sufficient to condense at least 30%, preferably at least 50%, up to 80% or 100%, of the $HSiO_{3/2}$ units to $SiO_{4/2}$ units. The temperature of the reaction with base can for example be in the range 0-140°C. For example, a 0.5M sodium acetate solution in aqueous MIBK will cause 50% conversion of $HSiO_{3/2}$ units to $SiO_{4/2}$ units at 100-110°C in about 1 hour. A 0.5M solution of sodium acetate in aqueous triethylamine will cause 50% conversion at 25°C in about 30-40 minutes. The process of the invention can be used to form a curable resin in which at least 5 mol%, preferably at least 20 or 30%, up to 50 or 55 mol% of the siloxane units of the resin are $SiO_{4/2}$ units. Resins having over 20% Q units can not easily be prepared directly from $SiCl_4$ or a tetraalkoxysilane without precipitation of silica.

[0016] The subsequent reaction of the resulting resin solution with a chlorosilane of the formula RR'_2SiCl converts most of the remaining Si-OH groups to Si-O-SiRR'$_2$ groups. The resin solution and chlorosilane are preferably reacted in the presence of a disilazane, which aids in the reaction of Si-OH groups. The disilazane is preferably a disilazane of the formula $RR'_2Si\text{-}NH\text{-}SiRR'_2$, in which the groups R and R' are the same as in the chlorosilane RR'_2SiCl. The reaction is preferably carried out under sustantantially anhydrous conditions in an organic solvent, for example a ketone having 4 to 7 carbon atoms and/or an aromatic hydrocarbon such as toluene or xylene. The reaction can be carried out at a temperature in the range 0-140°C, preferably 20-80°C. The reaction serves to introduce RR'_2Si- groups into the resin and to reduce the level of Si-OH. The concentration of -OH groups is generally reduced to below 2% by weight and usually below 1%, for example to 0.3-0.8%.

[0017] It is usually preferred that the starting resin comprising siloxane T units also comprises siloxane M units of the formula $RR'_2SiO_{1/2}$ since the reaction of the resin

solution with chlorosilane and optionally disilazane may not always introduce sufficient R groups to give the desired level of cure. Preferably, 5 to 40 mol% of the siloxane units of the curable resin are of the formula $RR'_2SiO_{1/2}$, most preferably at least 10 up to 30 mol%. If the group R is an alkenyl group, an alternative process according to the invention for the preparation of a curable silicone resin comprising siloxane M units of the formula $RR'_2SiO_{1/2}$, where R represents an alkenyl group having 1 to 6 carbon atoms and each R' represents an alkyl group having 1 to 4 carbon atoms or an aryl group, siloxane T units of the formula $ASiO_{3/2}$, where A represents an aryl group or an alkyl group having 1 to 4 carbon atoms, siloxane units of the formula $SiO_{4/2}$ and optionally siloxane T units of the formula $HSiO_{3/2}$, comprises treating a silicone resin comprising $RR'_2SiO_{1/2}$, $ASiO_{3/2}$, and $HSiO_{3/2}$ in solution with a base to condense at least some of the $HSiO_{3/2}$ units to form $SiO_{4/2}$ units. An analogous process can be used where R represents hydrogen atom, but this is not preferred because at least some of the $HR'_2SiO_{1/2}$ groups may be converted to $R'_2SiO_{2/2}$ groups. $HR'_2SiO_{1/2}$ groups in a curable resin are preferably formed by reaction of the resin solution with HR'_2SiCl.

[0018] The curable resin of the invention can be a self-curable resin in which R represents an alkenyl group and the resin also contains $HSiO_{3/2}$ units, for example where 10 to 50 mol% of the siloxane units of the resin are $HSiO_{3/2}$ units and preferably 5 to 40 mol% of the siloxane units of the resin are of the formula $RR'2SiO_{1/2}$ where R is alkenyl, most preferably vinyl. Such a self-curable resin can be prepared by reacting a chlorosilane of the formula $ArSiCl_3$ and dimethylvinylchlorosilane with trichlorosilane $HSiCl_3$ in the presence of water and a dipolar aprotic solvent, followed by treating the silicone resin produced in solution with a base to condense at least some of the $HSiO_{3/2}$ units to form $SiO_{4/2}$ units, and reacting the resulting resin solution with dimethylvinylchlorosilane. The proportion of $HSiCl_3$ reacted is selected to be sufficient to provide the desired level of $SiO_{4/2}$ units as well as the desired level of $HSiO_{3/2}$ units to form a self-curable resin. Such a self-curable silicone resin can be cured to a heat resistant silicone resin having a low coefficient of thermal expansion by heating in the presence of a catalyst containing a platinum group metal.

[0019] The curable resin generally has a molecular weight of at least 1000 up to 100000 or even higher, for example in the range 1500 to 220000. The treatment of the resin with a base to condense at least some of the $HSiO_{3/2}$ units to form $SiO_{4/2}$ units generally increases the molecular weight of the resin, so that resins of high Q content often have relatively high molecular weight.

[0020] A cured heat resistant silicone resin having a low coefficient of thermal expansion can be produced by reacting a curable silicone resin as described above with a curing agent having at least one functional group reactive with the group R. Where the group R is an alkenyl group, the curing agent preferably contains at least one Si-H group and the curing process is carried out in the presence of a catalyst containing a platinum group metal. The curing agent can for example be a polysiloxane containing at least two Si-H groups, such as a polydimethylsiloxane having terminal HR''_2Si- groups where R" is an alkyl group, preferably methyl, or phenyl group, for example $HMe_2Si\text{-}(O\text{-}SiMe_2)_4\text{-}O\text{-}SiMe_2H$ ($M^HD_4M^H$), or a polymethylhydrogensiloxane such as 1,3,5,7-tetramethylcyclotetrasiloxane ($D^{H,Me}{}_4$), or a silicone resin containing HR''_2Si- groups and T or Q units, for example a low molecular weight MQ resin containing HMe_2Si- groups such as $(HMe_2SiO_{1/2})_8(SiO_{4/2})_8$ ($M^H{}_8Q_8$). The curing agent can alternatively be an organic compound containing SiH groups, particularly HMe_2Si- groups, such as 1,4-bis(dimethylsilyl)benzene.

[0021] Where the group R is hydrogen, the curing agent preferably contains at least one alkenyl group and the curing process is preferably carried out in the presence of a catalyst containing a platinum group metal. The curing agent can for example be a polysiloxane containing at least two alkenyl, preferably vinyl groups such as a polydimethylsiloxane having terminal or pendant vinyl groups, for example 1,3-divinyltetramethyldisiloxane or hexavinyldisiloxane or 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane ($D^{Vi,Me}{}_4$), or a silicone resin containing RR''_2Si- groups where R is alkenyl, particularly $ViMe_2Si$- groups, and T or Q units, for example low molecular weight resins such as

$(ViMe_2SiO_{1/2})_3.PhSiO_{3/2}$ ($M^{Vi}{}_3T^{Ph}$) or $(ViMe_2SiO_{1/2})_4.SiO_{4/2}$ ($M^{Vi}{}_4Q$), or an alkenyl-substituted silane such as tetravinylsilane. The curing agent can alternatively be an organic compound such as 1,7-octadiene or divinylbenzene.

[0022] The curing catalyst is preferably a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex which can be used at 20 to 200, for example about 50, parts per million Pt based on the SiH-containing resin (mol/mol). Alternative curing catalysts can be used, for example chloroplatinic acid or an analogous rhodium compound.

[0023] The curing reaction is generally carried out at a temperature of at least 50°C, preferably at least 100°C, for example in the range 150 to 300°C, particularly 150 to 200°C.

[0024] The molecular weight of the curable resin can be controlled by controlling the condensation of $HSiO_{3/2}$ units to $SiO_{4/2}$ units, leading to a flowable or a solid resin at room temperature. In a process according to the invention for encapsulating a substrate, the substrate is encapsulated in a curable silicone resin according to the invention and the resin is then cured. Such a process can be used for encapsulating delicate substrates, particularly for microelectronic device packaging in processes such as Flip Chip Underfill, No Flow Fluxing Underfill or moulding encapsulation, and may for example replace epoxy or polyimide resins in such applications.

[0025] In a process according to the invention for coating a substrate, a curable silicone resin according to the invention is applied as a thin film to a substrate before being cured. Such a process can be used in coatings such as wafer level and solar panel coatings, in planarization layers for Flat Panel Displays and in photonic devices. Good quality thin films between 600 nm to 1.5 μm thick can be produced, as can thick free-standing films several mm. thick.

[0026] In a process according to the invention for fabricating composite panels and laminates, a fibrous material is impregnated with a curable silicone resin according to the invention and the resin is cured under the conditions described above.

[0027] Cured silicone resins according to the invention are generally heat resistant and have a coefficient of thermal expansion of 120 ppm/°C or below, measured for example over the temperature range 0 to 70°C. The CTE can be further reduced by the incorporation of a low CTE filler in the resin, for example silica, alumina or mica. The level of filler can for example be up to 200% by weight based on the silicone resin, preferably at least 5% up to 100%, for example 25 to 80% by weight. The filler is mixed with the curable resin according to the invention before curing. Incorporation of a low CTE filler can reduce the CTE of the filled resin below 50 ppm/°C, even to 20 ppm/°C or below.

[0028] In a preferred process according to the invention, the cured silicone resin is subsequently further heat cured at a temperature in the range 300 to 500°C. The further heat curing at 300-500°C produces crack-free cured resin exhibiting enhanced thermo-mechanical properties such as higher Young's modulus, even lower CTE, for example below 100 ppm/°C, higher plateau modulus (the minimum value of the Young's modulus over a temperature range of -100 to +300°C including the glass transition temperature Tg, most often within a plateau region at temperatures higher than Tg) and good retention of film quality and strength.

[0029] The further heating step at 300-500°C is preferably carried out in a non-oxidising atmosphere, for example it can be carried out under an inert gas such as nitrogen. Most preferably the further heating step at 300-500°C is carried out in the presence of an amine which is in the vapour state at the temperature of the further heating step. The amine is preferably a tertiary amine; it can for example be a tertiary amine of the formula NZ_3, where each Z represents an alkyl group having 1 to 4 carbon atoms.

[0030] The invention is illustrated by the following Examples

Example 1: Preparation of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ resin.

[0031] 150g (0.71 mol) of phenyltrichlorosilane and 96g (0.71 mol) of trichlorosilane were mixed into 290 ml of MIBK, and added dropwise into a solution consisting of 290ml of a 1M HCl aqueous solution, 500ml toluene and 500ml MIBK at room temperature over a 1h period. The mixture was aged for another hour at room temperature under constant stirring. The aqueous layer was poured off and the organic layer was washed four times with water until neutral pH. 300ml of 1 M aqueous solution of sodium acetate was added into the organic layer and the solution was mixed at room temperature for 1 hour under constant stirring. The aqueous phase was poured off and the organic layer was washed four times with water until neutral pH. The mixture was treated by anhydrous $NaSO_4$ to remove residual water by further centrifugation. The solvents were stripped off leading to a viscous liquid. This liquid was re-dissolved into 1000ml of anhydrous toluene and 3.09g (38.2 mmol) of dimethylchlorosilane and 3.98g (38.2 mmol) of 1,1,3,3-tetramethyl disilazane were added. The mixture was stirred at room temperature overnight. The organic layer was collected and washed four times with water until neutral pH. The mixture was again treated by anhydrous $NaSO_4$ to remove residual water by further centrifugation and the solvents were stripped off leading to 154g of a soft solid. The $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ composition of this resin was determined by ^{29}Si and ^{13}C NMR spectroscopy (Mn = 3,031; Mw = 7,652, OH wt % < 0.8%).

Example 2. Preparation of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ resin.

[0032] 60.00g (284 mmol) of phenyltrichlorosilane, 88.78g (655 mmol) of trichlorosilane and 47.52g (394 mmol) of dimethylvinylchlorosilane were dissolved into 240ml of MIBK, then added dropwise into a mixture consisting of 240ml of a 1M HCl aqueous solution, 360ml toluene and 480ml MIBK at room temperature over a 1h period. The mixture was refluxed at 110°C for another 3 hours under constant stirring. The organic layer was collected and washed four times with water until neutral pH. 240ml of a 1M sodium acetate (NaOAc) aqueous solution was added and the mixture was heated at 80 to

$90^{O}C$ for a further 3 days under constant stirring. The organic layer was collected and washed four times with water. Removal of residual water by anhydrous $NaSO_4$, and stripping off the solvent led to 93g of soft solid being highly soluble in common organic solvents. The $M^{ViMe2}{}_{0.24}T^{Ph}{}_{0.25}T^{H}{}_{0.13}Q_{0.38}$ composition of this resin was determined by ^{29}Si and ^{13}C NMR spectroscopy. To this solid, re-dissolved into 100ml of anhydrous toluene, was added at room temperature and under stirring 6.6g (54.8 mmol) of dimethylvinylchlorosilane and 10.1g (54.7 mmol) of 1,3-divinyl-1,1,3,3-tetramethyldisilazane. The mixture was heated from 40 to $60^{O}C$ for 2 hours. The organic layer was collected and washed four times with water until neutral pH. The mixture was treated by anhydrous $MgSO_4$ to remove residual water and the volatiles were stripped off leading to 88g of a soft solid. The $M^{ViMe2}{}_{0.28}T^{Ph}{}_{0.24}T^{H}{}_{0.13}Q_{0.35}$ resin composition of this resin was determined by ^{29}Si and ^{13}C NMR spectroscopy (Mn = 2,022; Mw = 7,276, OH wt % < 0.3%).

Example 3: Preparation of $M^{ViMe2}{}_{0.23}T^{Ph}{}_{0.26}T^{H}{}_{0.42}Q_{0.09}$ resin.

[0033] 50.0g (236 mmol) of phenyltrichlorosilane, 73.98g (546 mmol) of trichlorosilane and 39.6g (323 mmol) of dimethylvinylchlorosilane were dissolved into 240ml of MIBK, and then added dropwise into a mixture consisting of 240ml of a 1M HCl aqueous solution, 360ml toluene and 480ml MIBK at room temperature over a 1h period. The mixture was refluxed at 100°C for another 3 hours under constant stirring. The organic layer was isolated and washed four times with water until neutral pH. Removal of residual water by anhydrous $NaSO_4$, and stripping off the solvent led to 92g of a light yellow viscous liquid being highly soluble in common organic solvents. The $M^{ViMe2}{}_{0.23}T^{Ph}{}_{0.26}T^{H}{}_{0.42}Q_{0.09}$ composition of this resin was determined by ^{29}Si and ^{13}C NMR spectroscopy. (Mn = 1,375; Mw = 2,509).

Example 4: Preparation of $M^{ViMe2}{}_{0.20}T^{Ph}{}_{0.48}T^{H}{}_{0.12}Q_{0.20}$ resin.

[0034] 41.15g (196 mmol) of phenyltrichlorosilane, 23.18g (171 mmol) of trichlorosilane and 14.74g (122 mmol) of dimethylvinylchlorosilane were dissolved into

135ml of MIBK, then added dropwise into a mixture consisting of 135ml of a 1M HCl aqueous solution, 135ml toluene and 270ml MIBK at room temperature over a period of 45 minutes. The mixture was refluxed at 110°C for another 3 hours under constant stirring. The organic layer was isolated and washed four times with water until neutral pH. 300ml of a 1M sodium acetate aqueous solution was added into the organic layer and the mixture was heated at 40°C over 6 days under constant stirring. The organic layer was isolated again and washed four times with water until neutral pH. Removal of residual water by anhydrous $NaSO_4$, and stripping off the solvent led to 67.8g of a light yellow soft solid being highly soluble in common organic solvents. The $M^{ViMe2}_{0.20}T^{Ph}_{0.48}T^{H}_{0.12}Q_{0.20}$ composition of this resin was determined by ^{29}Si and ^{13}C NMR spectroscopy (Mn = 1,490; Mw = 2,765).

Example 5: Preparation of $M^{HMe2}_{0.02}M^{ViMe2}_{0.18}T^{Ph}_{0.35}T^{H}_{0.23}Q_{0.22}$ resin.

[0035] 57.75g (273 mmol) of phenyltrichlorosilane, 61.65g (455 mmol) of trichlorosilane and 22.0g (182 mmol) of dimethylvinylchlorosilane were dissolved into 200ml of MIBK, and added dropwise into a mixture consisting of 200ml of a 1M HCl aqueous solution, 300ml toluene and 400ml MIBK at room temperature over a 1h period. The mixture was refluxed at 100°C for another 3 hours under constant stirring. The organic layer was isolated and washed four times with water until neutral pH. 300ml of a 1.M sodium acetate aqueous solution was added into the organic layer and the mixture was heated at 70°C over 18h under constant stirring. The organic layer was isolated again and washed four times with water until neutral pH. Removal of residual water by anhydrous $NaSO_4$, and stripping off the solvent led to 74.62g of a soft solid being highly soluble in common organic solvents. The $M^{ViMe2}_{0.17}T^{Ph}_{0.34}T^{H}_{0.22}Q_{0.27}$ composition of this resin was determined by ^{29}Si and ^{13}C NMR spectroscopy (Mn = 2,428; Mw = 5,535). 46.64g of $M^{ViMe2}_{0.17}T^{Ph}_{0.34}T^{H}_{0.22}Q_{0.27}$ were then dissolved into 500ml anhydrous toluene, 1.18g (12.5 mmol) of dimethylchlorosilane and 1.67g (12.5 mmol) of 1,1,3,3-tetramethyldisilazane. This mixture was stirred at 40°C for 2h. The organic layer was isolated and washed with an HCl solution, and subsequently washed four times with water until neutral pH. Removal of residual water by anhydrous $NaSO_4$, and stripping off the solvent led to 46.5g of a soft solid. The

$M^{HMe2}_{0.02}M^{ViMe2}_{0.18}T^{Ph}_{0.35}T^{H}_{0.23}Q_{0.22}$ composition of this resin was determined by ^{29}Si and ^{13}C NMR spectroscopy. (Mn = 2,456; Mw = 5,458).

Example 6: Preparation of $M^{ViMe2}_{0.22}T^{Ph}_{0.27}T^{H}_{0.15}Q_{0.36}$ resin.

[0036] To a toluene/MIBK mixture of $M^{ViMe2}_{0.23}T^{Ph}_{0.26}T^{H}_{0.42}Q_{0.09}$ prepared according to example 3, was added 360ml of a 1M sodium acetate solution. The mixture was heated at 90°C for 16hr under constant stirring. The organic layer was isolated and washed four times with water until neutral pH. Removal of residual water by anhydrous $NaSO_4$, and stripping off the solvent led to 95g of a soft liquid, being highly soluble in common organic solvents. The $M^{ViMe2}_{0.22}T^{Ph}_{0.27}T^{H}_{0.15}Q_{0.36}$ composition of this resin was determined by ^{29}Si and ^{13}C NMR spectroscopy. (Mn = 2,125; Mw = 6,299).

Example 7: Cure of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ with $M^{Vi}_{3}T^{Ph}$.

[0037] To 3.3 g of a 60.1 wt% solution of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ resin (example 1) in toluene, and 1.4 g of $M^{Vi}_{3}T^{Ph}$ was added 0.2 g of a 10 wt% solution of a platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene ($Pt^{O}/SiH = 50$ ppm). The mixture was poured into a mould for gradual heating up to 200°C for 3h. The final material was analysed by DMTA and thermomechanical analysis (TMA) (Table 1).

Example 8: Cure of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ with $D^{Vi,Me}_{4}$.

[0038] To 4.0 g of a 60.1 wt% solution of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ resin (example 1) in toluene, and 1.1 g of $D^{Vi,Me}_{4}$ was heated at 90°C prior to addition of 0.2 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene ($Pt^{O}/SiH = 50$ ppm). The mixture was kept at 90°C for 15 minutes and the advancement of the cure was followed by FTIR. The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 9: Cure of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ with M^{ViMe2}_{2}.

[0039] To 5.0 g of a 60.1 wt% solution of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ resin (example 1) in toluene, and 1.5 g of 1,3-divinyltetramethyldisiloxane was heated at 90°C prior to addition of 0.3 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^{O}/SiH = 50 ppm). The mixture was kept at 90°C for 1h and the advancement of the cure was followed by FTIR. The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 10: Cure of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ with $M^{Vi}_{4}Q$.

[0040] To 3.3 g of a 60.1 wt% solution of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ resin (example 1) in toluene, and 1.1 g of $M^{Vi}_{4}Q$ was heated at 90°C prior to addition of 0.19 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^{O}/SiH = 50 ppm). The mixture was kept at 90°C for 15 minutes and the advancement of the cure was followed by FTIR. The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 11: Cure of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ with M^{Vi3}_{2}.

[0041] To 6.0 g of a 60.1 wt% solution of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ resin (example 1) in toluene, and 0.7 g of hexavinyldisiloxane was heated at 90°C prior to addition of 0.2 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^{O}/SiH = 50 ppm). The mixture was kept at 90°C for 10 minutes and the advancement of the cure was followed by FTIR. The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 12: Cure of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ with $SiVi_4$.

[0042] To 6.0 g of a 60.1 wt% solution of $M^{HMe2}_{0.07}T^{Ph}_{0.45}T^{H}_{0.40}Q_{0.08}$ resin (example 1) in toluene, and 0.7 g of tetravinylsilane was heated at 90°C prior to addition of 0.3 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^O/SiH = 50 ppm). The mixture was kept at 90°C for 10 minutes and the advancement of the cure was followed by FTIR. The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 13: Cure of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ with $M^{H}D_4M^{H}$.

[0043] To 4.0 g of a 86.4 wt% solution of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ resin (example 2) in toluene, was added under stirring 2.0 g of $M^{H}D_4M^{H}$ and 0.3 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^O/SiH = 50 ppm). The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 14: Cure of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ with 1,4-bis(dimethylsilyl)benzene.

[0044] To 4.0 g of a 86.4 wt% solution of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ resin (example 2) in toluene, was added under stirring 0.9 g of 1,4-bis(dimethylsilyl)benzene and 0.3 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^O/SiH = 50 ppm). The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 15: Cure of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ with $M^{H}_3T^{Ph}$.

[0045] To 4.0 g of a 86.4 wt% solution of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ resin (example 2) in toluene, was added under stirring 1.0 g of $M^{H}_3T^{Ph}$ and 0.3 g of a 10 wt%

solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^O/SiH = 50 ppm). The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 16: Cure of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ with $D^{H,Me}_{4}$.

[0046] To 4.0 g of a 86.4 wt% solution of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ resin (example 2) in toluene, was added under stirring 0.6 g of $D^{H,Me}_{4}$ and 0.3 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^O/SiH = 50 ppm). The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 17: Cure of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ with $M^{H}_{8}Q_{8}$.

[0047] To 4.0 g of a 86.4 wt% solution of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ resin (example 2) in toluene, was added under stirring 1.2 g of $M^{H}_{8}Q_{8}$, 0.3 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^O/SiH = 50 ppm) and 4.0 g of anhydrous toluene. The mixture was poured into a mould for gradual heating up to 200°C for 3h.

Example 18 to 23: Self-addition cure of $M^{ViMe2}_{v}M^{HMe2}_{w}T^{Ph}_{x}T^{H}_{y}Q_{z}$ resins.

[0048] Self-addition curable silicone resins (examples 3 to 6) were subjected to addition cure using a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene as the catalyst. A typical experimental procedure is as follow: the resin was dissolved in anhydrous toluene and then mixed with a catalytic amount of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^O/SiH = 50 ppm) for 10 minutes to a 75 wt% solution before casting into a mould. The samples were then heated gradually up to 150 or 200°C for 3h.

[0049] The cured resins produced by each of Examples 7 to 23 were analysed by DMTA and TMA and the results are shown in Table 1, in which E'_{25} is the modulus at 25°C or Young's modulus and E'_p is the plateau modulus. The CTE of the cured resins was measured over various temperature ranges shown in °C.

Table 1. Thermo-mechanical analysis of cured materials.

Entry	Resin composition before cure#	Mw	X-linker	Cure Temp. (°C)	E'_{25} (MPa)	E'_p (MPa)	CTE (ppm/°C)
Example 7	$M^{HMe2}{}_{0.07}T^{Ph}{}_{0.45}T^{H}{}_{0.40}Q_{0.08}$	7,652	$M^{Vi}{}_3T^{Ph}$	200	1,250	450	82 (-80/-20), 104 (-20/0), 119 (0/60), 171 (60/170), 204 (170/200)
Example 8			$D^{Vi, Me}{}_4$		1,480	810	87 (-80/-20), 115(-20/100), 206 (120/150)
Example 9			$(M^{Me2Vi})_2$		2,060	860	85 (-80/0), 108 (0/70), 144 (70/100), 163 (100/170)
Example 10			$M^{Vi}{}_4Q$		1,550	1,040	45 (-80/-40), 75 (-30/0), 98 (0/60), 125 (70/140), 123 (195/245)

Entry	Resin composition before cure#	Mw	X-linker	Cure Temp. (°C)	E'25 (MPa)	E'p (MPa)	CTE (ppm/°C)
Example 11			$(M^{Vi3})_2$		2,070	1,200	64 (-80/0), 93 (0/40), 122 (40/70), 173 (70/100), 197 (100/199)
Example 12			$SiVi_4$		2,280	1,250	67 (-80/0), 77 (0/90), 158 (110/180)
Example 13	$M^{ViMe2}{}_{0.28}T^{Ph}{}_{0.24}T^{H}{}_{0.13}Q_{0.35}$	7,276	$M^HD_4M^H$		440	420	141 (-80/-40), 173 (-30/0), 190 (0/70), 200 (80/140), 252 (140/166), 177 (205/240)
Example 14			$(HMe_2Si)_2Ph$		2,430	660	61 (-80/-40), 75 (-30/0), 95 (0/50), 128 (50/110), 170 (110/140), 192 (140/154), 155 (197, 235)
Example 15			$M^H{}_3T^{Ph}$		1,410	890	70 (-80/-30), 96 (-30/0), 136 (0/70), 152 (80/140), 158 (140/170), 168 (180/200)

Entry	Resin composition before cure#	Mw	X-linker	Cure Temp. (°C)	E'25 (MPa)	E'p (MPa)	CTE (ppm/°C)
Example 16	$M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$	7276	$D^{H,Me}_{4}$		1,270	1,010	68 (-80/-40), 90 (-30/0), 112 (0/70), 123 (80/165), 90 (200/245)
Example 17			$M^{H}_{8}Q_{8}$		1,850	1,620	67 (-80/-40), 92 (-30/0), 115 (0/50), 126 (70/140), 139 (140/160), 102 (190/230)
Example 18	$M^{ViMe2}_{0.23}T^{Ph}_{0.26}T^{H}_{0.42}Q_{0.09}$	2,509	None	200	1,870	620	66 (-80/0), 69 (0/70), 84 (70/100), 126 (100/240)
Example 19	$M^{ViMe2}_{0.20}T^{Ph}_{0.48}T^{H}_{0.12}Q_{0.20}$	2,765		200	1,475	727	59 (-80/0), 70 (0/70), 98 (70/100), 108 (100/150)
Example 20	$M^{ViMe2}_{0.18}M^{HMe2}_{0.02}T^{Ph}_{0.35}T^{H}_{0.23}Q_{0.22}$	5,458		150	921	412	73 (-80/0), 96 (0/70), 125 (70/100), 152 (100/200), 134 (200/240)

Entry	Resin composition before cure#	Mw	X-linker	Cure Temp. (°C)	E'25 (MPa)	E'p (MPa)	CTE (ppm/°C)
Example 21				200	1,550	1,020	64 (-80/-50), 81 (-50/30), 105 (30/70), 121 (70/100), 133 (100/240)
Example 22	$M^{ViMe2}_{0.22}T^{Ph}_{0.27}T^{H}_{0.15}Q_{0.36}$	6,299		150	1,018	554	73 (-80/0), 105 (0/70), 145 (70/100), 158 (100/150), 141 (160/220)
Example 23				200	2,060	1,600	64 (-80/-60), 82 (-60/30), 121 (40/190)

Examples 24 and 25. Preparation of $M^{ViMePh}_{0.15}T^{Ph}_{0.25}T^{H}_{0.60-x}Q_x$ resin series by IQG process

[0050] 19.29g (91.2 mmol) of phenyltrichlorosilane, 29.66g (218.9 mmol) of trichlorosilane and 10.00g (54.7 mmol) of phenylmethylvinylchlorosilane were dissolved into 100ml of MIBK, then added dropwise into a mixture consisting of 100ml of water, 150ml of toluene and 200ml of MIBK, at room temperature over a 1h period. The mixture was refluxed at 110°C for another 2 hours under constant stirring. The organic layer was collected and washed four times with water until neutral pH. 200ml 0.1M sodium acetate (NaOAc) aqueous solution was added and the mixture was refluxed at 110°C. Samples were collected from the organic layer at various reaction times, leading to $M^{ViMePh}_{0.15}T^{Ph}_{0.25}T^{H}_{0.60-x}Q_x$ resins series compositions. After washing the samples four times, stripping off the residual water and solvent, approximately 5.5 to 6.5g of white solids were obtained for each resin

portion. Resin compositions were determined by ^{29}Si and ^{13}C NMR whereas molecular weights were determined by GPC (Table 2).

Table 2. $M^{ViMePh}{}_{0.15}T^{Ph}{}_{0.25}T^{H}{}_{0.60-x}Q_x$ resin compositions.

	Conversion Time	% T^H into Q conversion	Composition	Mn	Mw
	0 hr	0	$M^{ViMePh}{}_{0.15}T^{Ph}{}_{0.25}T^{H}{}_{0.60}$	820	3,810
Example 24	1 day	25	$M^{ViMePh}{}_{0.15}T^{Ph}{}_{0.25}T^{H}{}_{0.45}Q_{0.15}$	1,260	4,400
Example 25	6 days	75	$M^{ViMePh}{}_{0.15}T^{Ph}{}_{0.25}T^{H}{}_{0.15}Q_{0.45}$	1,770	38,400

[0051] The resins of Examples 24 and 25 could be cured using the curing agents of Examples 13 to 17 to give cured resins of low CTE.

Example 26: Cure of $M^{ViMe2}{}_{0.23}T^{Ph}{}_{0.26}T^{H}{}_{0.42}Q_{0.09}$ with 1,4-bis(dimethylsilyl)benzene.

[0052] To 3.7 g of $M^{ViMe2}{}_{0.23}T^{Ph}{}_{0.26}T^{H}{}_{0.42}Q_{0.09}$ resin prepared as described in Example 3 was added under stirring 1.0g of 1,4-bis(dimethylsilyl)benzene and 0.43 ml of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in toluene (Pt^O/SiH = 50 ppm). The mixture was sonicated and poured into a mould for gradual heating up to 200°C for 3h.

Example 27: Preparation of $M^{ViMe2}{}_{0.20}T^{Ph}{}_{0.35}T^{H}{}_{0.21}Q_{0.24}$ resin.

[0053] 57.75g (273 mmol) of phenyltrichlorosilane, 61.65g (455 mmol) of trichlorosilane and 22.0g (182 mmol) of dimethylvinylchlorosilane were dissolved into 200ml

of MIBK, and added dropwise into a mixture consisting of 200ml of a 1M HCl aqueous solution, 300ml toluene and 400ml MIBK at room temperature over a 1h period. The mixture was refluxed at 100°C for another 3 hours under constant stirring. The organic layer was isolated and washed four times with water until neutral pH. 300ml of a 1M sodium acetate aqueous solution was added into the organic layer and the mixture was heated at 70°C over 18h under constant stirring. The organic layer was isolated again and washed four times with water until neutral pH. Removal of residual water by anhydrous $NaSO_4$, and stripping off the solvent led to 74.62g of a soft solid being highly soluble in common organic solvents. This procedure was repeated 2 more times and the 3 fractions were mixed together to get 191.7g of $M^{ViMe2}{}_{0.17}T^{Ph}{}_{0.36}T^{H}{}_{0.23}Q_{0.24}$ resin composition as determined by ^{29}Si and ^{13}C NMR spectroscopy (OH wt %= 1.08%).

[0054] 191.7g of $M^{ViMe2}{}_{0.17}T^{Ph}{}_{0.36}T^{H}{}_{0.23}Q_{0.24}$ were then dissolved into 150ml anhydrous toluene, and 8.07g (67 mmol) of dimethylchlorosilane and 11.30g (69 mmol) of 1,1,3,3-tetramethyldisilazane were then added at room temperature. This mixture was further stirred at 40°C for 2h. The organic layer was isolated and washed with an HCl solution, and subsequently washed four times with water until neutral pH. Removal of residual water by anhydrous $NaSO_4$, and stripping off the solvent led to 191.5g of a white soft solid. The $M^{ViMe2}{}_{0.20}T^{Ph}{}_{0.35}T^{H}{}_{0.21}Q_{0.24}$ composition of this resin was determined by ^{29}Si and ^{13}C NMR spectroscopy (Mn = 2,227; Mw = 5,152, OH wt % < 0.8%).

Example 28: Cure of $M^{ViMe2}{}_{0.20}T^{Ph}{}_{0.25}T^{H}{}_{0.21}Q_{0.24}$ with 1,4-bis(dimethylsilyl)benzene.

[0055] To 5.0 g of a 73.7 wt% solution of $M^{ViMe2}{}_{0.20}T^{Ph}{}_{0.25}T^{H}{}_{0.21}Q_{0.24}$ resin (prepared as described in Example 27) in toluene, was added under stirring 0.79 g of 1,4-bis(dimethylsilyl)benzene and 0.3 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^{O}/SiH = 50 ppm). The mixture was sonicated and poured into a mould for gradual heating up to 200°C for 3h.

Example 29: Cure of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ with $D^{H,Me}_{4}$.

[0056] To 4.0 g of a 86.4 wt% solution of $M^{ViMe2}_{0.28}T^{Ph}_{0.24}T^{H}_{0.13}Q_{0.35}$ resin (prepared as described in Example 2) in toluene, was added under stirring 0.6 g of $D^{H,Me}_{4}$ and 0.3 g of a 10 wt% solution of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt^{O}/SiH = 50 ppm). The mixture was poured into a mould for gradual heating up to 200^{O}C for 3h.

Example 30: Self-addition cure of $M^{ViMe2}_{0.20}T^{Ph}_{0.25}T^{H}_{0.21}Q_{0.24}$

[0057] The curable silicone resin of Example 27 was subjected to addition cure using a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene as the catalyst. The resin was dissolved in anhydrous toluene and then mixed with a catalytic amount of a platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in toluene (Pt°/SiH = 50 ppm) for 10 minutes to a 75 wt% solution before casting into a mould. The samples were then heated gradually up to 200^{O}C for 3h.

Examples 31 to 36: thermal post-cure

[0058] Addition-cured free-standing resin films produced by the process of each of Examples 8, 26, 28, 29, 18 and 30 were subjected to an annealing treatment as follows: The addition-cured free-standing resin film was placed into the chamber of a furnace. The chamber was purged by 3 vacuum/N_2 cycles. The samples were then heated under N_2 gradually up to 400°C. The N_2 inlet was then bubbled through a triethylamine solution and the samples were further heated at 400°C for 2 hours under a N_2/triethylamine vapour atmosphere. Crack-free specimens were obtained. The post-cured samples, and the cured resin films from which they were obtained, were analysed by DMTA and TMA, and the results are shown in Table 3.

Table 3

Example	Resin of Example	X-linker	Cure Temp. (°C)	E'$_{25}$ (MPa)	E'$_{p}$ (Mpa)	CTE (ppm/K) (temp. range in °C)
8	1	$D^{Vi, Me}_4$	200	1,480	810	87 (-80/-20), 115 (-20/100), 206 (120/150)
31		/	400	2,530	2,030	61 (-80/-40), 77 (-30/0), 84 (0/70), 111 (80/140), 128 (140/165)
26	3	$(HMe_2Si)_2Ph$	200	2,110	290	63 (-80/-40), 84 (-30/0), 96 (0/70), 201 (140/170)
32		/	400	2,540	1,420	57 (-80/-40), 79 (-30/0), 87 (0/70), 124 (80/140), 155 (140/185)
28	27	$(HMe_2Si)_2Ph$	200	2,670	830	59 (-80/-40), 72 (-30/0), 92 (0/70), 130 (80/140), 199 (140/175)
33		/	400	2,400	1,220	54 (-80/-40), 78 (-30/0), 65 (0/70), 139 (140/170)
29	2	$D^{H,Me}_4$	200	1,270	1,010	68 (-80/-40), 90 (-30/0), 112 (0/70), 123 (80/165), 90 (200/245)
34		/	400	1,960	1,630	62 (-80/-40), 86 (-30/0), 94 (0/70), 102 (80/140), 112 (140/170)
18	3	None	200	1,870	620	66 (-80/0), 69 (0/70), 84 (70/100), 126 (100/240)

Example	Resin of Example	X-linker	Cure Temp. (^oC)	E'_{25} (MPa)	E'_p (Mpa)	CTE (ppm/K) (temp. range in °C)
35		None	400	2,010	1,830	64 (-80/-40), 82 (-30/0), 88 (0/70), 93 (80/140), 99 (140/170)
30	27		200	1,930	1,370	72 (-80/-40), 86 (-30/0), 105 (0/70), 128 (80/140), 150 (140/190)
36			400	2,670	1,860	64 (-80/-40), 83 (-30/0), 79 (0/70), 116 (80/140), 118 (140/165)

[0059] As can be seen from Table 3, the cured resins produced by post-curing at 400°C had increased Young's modulus, decreased CTE and showed a particularly high increase in plateau modulus.

CLAIMS

1. A curable silicone resin comprising siloxane units of the formula $RR'_2SiO_{1/2}$, where R represents a hydrogen atom or an alkenyl group having 1 to 6 carbon atoms and each R' represents an alkyl group having 1 to 4 carbon atoms or an aryl group, siloxane units of the formula $ArSiO_{3/2}$, where Ar represents an aryl group, siloxane units of the formula $SiO_{4/2}$ and optionally siloxane units of the formula $HSiO_{3/2}$.

2. A curable silicone resin according to Claim 1 wherein R represents a vinyl group.

3. A curable resin according to Claim 1 or Claim 2 wherein 5 to 40 mol% of the siloxane units of the resin are of the formula $RR'_2SiO_{1/2}$.

4. A curable resin composition according to any of Claims 1 to 3 wherein Ar represents a phenyl group and 5 to 70 mol% of the siloxane units of the resin are of the formula $ArSiO_{3/2}$.

5. A curable resin composition according to any of Claims 1 to 4 wherein 20 to 55 mol% of the siloxane units of the resin are $SiO_{4/2}$ units.

6. A self-curable resin according to any of Claims 1 to 5 wherein R represents an alkenyl group and 10 to 50 mol% of the siloxane units of the resin are $HSiO_{3/2}$ units.

7. A process for the preparation of a curable silicone resin comprising siloxane units of the formula $RR'_2SiO_{1/2}$, where R represents a hydrogen atom or an alkenyl group having 1 to 6 carbon atoms and each R' represents an alkyl group having 1 to 4 carbon atoms or an aryl group, siloxane units of the

formula $ASiO_{3/2}$, where A represents an aryl group or an alkyl group having 1 to 4 carbon atoms, siloxane units of the formula $SiO_{4/2}$ and optionally siloxane units of the formula $HSiO_{3/2}$, characterised in that a silicone resin comprising siloxane units of the formula $ASiO_{3/2}$ and $HSiO_{3/2}$ and optionally $RR'_2SiO_{1/2}$ is treated in solution with a base to condense at least some of the $HSiO_{3/2}$ units to form $SiO_{4/2}$ units, and the resulting resin solution is reacted with a chlorosilane of the formula RR'_2SiCl.

8. A process according to Claim 7 characterised in that the resin solution and chlorosilane are reacted in the presence of a disilazane.

9. A process for the preparation of a curable silicone resin comprising siloxane units of the formula $RR'_2SiO_{1/2}$, where R represents an alkenyl group having 1 to 6 carbon atoms and each R' represents an alkyl group having 1 to 4 carbon atoms or an aryl group, siloxane units of the formula $ASiO_{3/2}$, where A represents an aryl group or an alkyl group having 1 to 4 carbon atoms, siloxane units of the formula $SiO_{4/2}$ and optionally siloxane units of the formula $HSiO_{3/2}$, characterised in that a silicone resin comprising $RR'_2SiO_{1/2}$, $ASiO_{3/2}$, and $HSiO_{3/2}$ units is treated in solution with a base to condense at least some of the $HSiO_{3/2}$ units to form $SiO_{4/2}$ units.

10. A curable silicone resin produced by the process of any of Claims 7 to 9.

11. A process for the preparation of a cured heat resistant silicone resin having a low coefficient of thermal expansion, characterised in that a curable silicone resin according to any of Claims 1 to 6 or 10 is reacted with a curing agent having at least one functional group reactive with the group R.

12. A process according to Claim 11, characterised in that the group R is an alkenyl group, the curing agent contains at least one Si-H group and the curing process is carried out in the presence of a catalyst containing a platinum group metal.

13. A process according to Claim 11, characterised in that the group R is hydrogen, the curing agent contains at least one alkenyl group and the curing process is carried out in the presence of a catalyst containing a platinum group metal.

14. A process according to any of Claims 11 to 13, characterised in that the curable silicone resin according to any of Claims 1 to 6 or 10 is reacted at a temperature in the range 50 to 300°C with the curing agent having at least one functional group reactive with the group R, and is subsequently further heat cured at a higher temperature in the range 300 to 500°C.

15. A process for the preparation of a cured heat resistant silicone resin having a low coefficient of thermal expansion, characterised in that a self-curable silicone resin according to Claim 6 is heated in the presence of a catalyst containing a platinum group metal.

16. A process according to Claim 15, characterised in that the self-curable silicone resin according to Claim 6 is cured at a temperature in the range 50 to 300°C in the presence of a catalyst for the reaction of alkenyl groups with Si-H groups, and is subsequently further heat cured at a higher temperature in the range 300 to 500°C.

17. A process according to Claim 14 or Claim 16, characterized in that the further heating step at 300-500°C is carried out in a non-oxidising atmosphere in the presence of an amine which is in the vapour state at the temperature of the further heating step.

18 A process according to Claim 17, characterized in that the amine is a tertiary amine of the formula NZ_3, where each Z represents an alkyl group having 1 to 4 carbon atoms.

19. A process for encapsulating a substrate, characterised in the substrate is encapsulated in a curable silicone resin according to any of Claims 1 to 6 or 10 and the resin is cured by a process according to any of Claims 11 to 18.

19. A process for coating a substrate, characterised in that the curable silicone resin according to any of Claims 1 to 6 or 10 is applied as a thin film to a substrate before being cured by a process according to any of Claims 11 to 18.

20. A process for fabricating composite panels and laminates, characterised in that a fibrous material is impregnated with a curable resin according to any of Claims 1 to 6 or 10 and the resin is cured by a process according to any of Claims 11 to 18.

21. A cured heat resistant silicone resin prepared by the process of any of Claims 11 to 20.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/02824

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D183/04 C08G77/08 C08G77/38 C08G77/12 C08K5/098
C08G77/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D C08G C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 446 087 A (CHIZAT FRANCOIS ET AL) 29 August 1995 (1995-08-29) column 1, line 47 -column 2, line 17; claim 1; example 1A	1-21
P,X	WO 02 081552 A (MACKINNON IAIN ;OU DUAN LI (GB); CHEVALIER PIERRE MAURICE (GB); DO) 17 October 2002 (2002-10-17) page 5, line 5 -page 7, line 20; claims 1-11; examples 30-32	1-21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 June 2003	13/06/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Contet, F

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/02824

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 5446087	A	29-08-1995	FR	2698875	A1	10-06-1994
			CA	2110750	A1	05-06-1994
			DE	69318118	D1	28-05-1998
			DE	69318118	T2	22-10-1998
			EP	0601938	A1	15-06-1994
			ES	2116425	T3	16-07-1998
			FI	935440	A	05-06-1994
			NO	934373	A	06-06-1994
WO 02081552	A	17-10-2002	WO	02081552	A1	17-10-2002

DERWENT-ACC-NO: 2003-853670

DERWENT-WEEK: 200432

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TITLE: Curable silicone resin for coating or encapsulating substrate in fabricating composite panels and laminates, comprises alkenyl-containing siloxane units, and aryl-containing siloxane units

INVENTOR: CHEVALIER P; DUPONT A ; OU D L ; ROBSON S

PATENT-ASSIGNEE: DOW CORNING CORP[DOWO]

PRIORITY-DATA: 2002GB-024043 (October 16, 2002) , 2002GB-006786 (March 22, 2002)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
WO 03080753 A1	October 2, 2003	EN
AU 2003219079 A1	October 8, 2003	EN

DESIGNATED-STATES: AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SC SD S E SG SK SL TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW AT BE BG CH CY CZ DE DK EA EE ES FI FR GB GH GM GR HU IE IT KE LS LU MC MW MZ NL OA PT RO SD SE SI SK SL SZ TR TZ UG ZM ZW

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO2003080753A1	N/A	2003WO-EP02824	March 17, 2003
AU2003219079A1	Based on	2003AU-219079	March 17, 2003

ABSTRACTED-PUB-NO: WO 03080753 A1

BASIC-ABSTRACT:

NOVELTY - A curable silicone resin comprises alkenyl-containing siloxane units, aryl-containing siloxane units, and other siloxane units.

DESCRIPTION - A curable silicone resin comprises a siloxane units of formula RR'2SiO1/2, siloxane units of ArSiO3/2, siloxane units of formula

SiO4/2, and optionally siloxane units of HSiO3/2.

R = H or 1-6C alkenyl;

R' = 1-4C alkyl or aryl;

Ar = aryl.

An INDEPENDENT CLAIM is also included for preparing a curable silicone resin comprising treating siloxane units of formula ASiO3/2 and HSiO3/2 and optionally RR'2SiO1/2 with a base to condense HSiO3/2 units and form SiO4/2 units, and resulting resin solution is reacted with a chlorosilane of formula RR'2SiCl.

USE - For coating or encapsulating a substrate in fabricating composite panels and laminates.

ADVANTAGE - The inventive resin can be cured to a heat resistant silicone resin having a low coefficient of thermal expansion (CTE). It includes SiO4/2 units that provide a silicon resin with lower CTE, increased glass transition temperature, and high thermal stability.

EQUIVALENT-ABSTRACTS:

POLYMERS

Preferred Compositions: The resin comprises 5-40 mol % siloxane units of formula RR'2SiO1/2, 20-55 mol% siloxane units of formula SiO-4/2, and 10-50 mol% siloxane units of formula HSiO3/2. Preferred Method: The curing process is carried out in the presence of catalyst containing platinum group metal. The reacting step is carried out at 50-300degreesC and heat curing is carried out in 300-

500degreesC. The heating step at 300-500degreesC is carried out in a non-oxidizing atmosphere in the presence of an amine, which is in the vapor state.

ORGANIC CHEMISTRY

Preferred Components: The curing agent contains alkenyl group with SiH. The amine is a tert-amine of formula NZ3, where Z is 1-4C atom.

Preferred Definitions:

R = vinyl or alkenyl;

Ar = Ph.

57.75 g Phenyltrichlorosilane, 61.65 g trichlorosilane, and 22 g dimethylvinylchlorosilane were dissolved in 200 ml of methyl isobutyl ketone (MIBK), and added dropwise with a mixture of 200 ml aqueous 1 M hydrochloric acid, 300 ml toluene, and 400 ml MIBK over 1 hour period. The mixture was refluxed at 100degreesC for 3 hours. The organic layer was neutralized, added with 300 ml of 1 M sodium acetate aqueous solution, and heated at 70degreesC over 18 hours. Residual water was removed and solvent was stripped off to provide a 74.62 g soft solid being highly soluble in common organic solvent. This procedure was repeated 2 more times to yield a resin composition, which was dissolved into 150 ml anhydrous toluene, and 8.08 g dimethylchlorosilane and added with 11.3 g 1,1,3,3-tetramethyldisilazane. This mixture was worked up to provide a curable silicone resin containing siloxane units with molecular weight of 5152, average number molecular weight of 2227 and hydroxide content of less than 0.8%.

TITLE-TERMS: CURE SILICONE RESIN COATING ENCAPSULATE SUBSTRATE FABRICATE COMPOSITE PANEL LAMINATE COMPRISE ALKENYL CONTAIN SILOXANE UNIT ARYL

DERWENT-CLASS: A26 A85 A89 G02 L03 U11 V07

CPI-CODES: A06-A00E1; A12-B01C; G02-A01A; L03-H04E1; L04-C20A; L04-C22;

EPI-CODES: U11-A07;

ENHANCED-POLYMER-INDEXING: Polymer Index [1.1]
018 ; D11 D10 D18*R D50 D82 D83 D84 D85 D86 D87 D88 F86; P1445*R F81 Si 4A; M9999 M2073; S9999 S1627 S1605;

Polymer Index [1.2]
018 ; G2288 G2277 G2266 D01 Si 4A D19 D18 D31 D76 D50 D86 F85 F86 Cl 7A; G2288 G2277 G2266 D01 Si 4A F83 F85 Cl 7A; G2288 G2277 G2266 D01 Si 4A D12 D10 D53 D51 D58 D84 F85 F86 Cl 7A; P1445*R F81 Si 4A; H0033 H0011; M9999 M2073; L9999 L2391; L9999 L2073; S9999 S1627 S1605;

Polymer Index [1.3]
018 ; ND01; B9999 B4988*R B4977 B4740; Q9999 Q7114*R; Q9999

Q7523; Q9999 Q7818*R;
K9676*R; K9483*R; N9999
N6779 N6735 N6655;
N9999 N6860 N6655;
B9999 B5618 B5572;
B9999 B5630 B3510
B3372; B9999 B5094
B4977 B4740; N9999
N6177*R; B9999 B5538
B5505; B9999 B4682
B4568; B9999 B4900
B4740;

Polymer Index [1.4]
018 ; D01 D11 D10 D50
D86 F23 R00836 786; D01
D02 D11 D10 D19 D18 D31
D50 D76 D87 R00862 26;
A999 A475; A999 A771;

Polymer Index [1.5]
018 ; D01 D12 D10 D51*R
F83; A999 A157*R;

Polymer Index [1.6]
018 ; G2277 G2266 D01
D11 D10 D50 D82 F83 F85
F86 Cl 7A R16680 1945;
A999 A157*R;

Polymer Index [1.7]
018 ; D01 D11 D10 D50
D84 F82 F83; A999
A157*R;

Polymer Index [1.8]
018 ; Pt 8B Tr; A999
A146;

Polymer Index [2.1]
018 ; A999 A157*R; A999 A782; P1445*R F81 Si 4A;

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: 2003-240623

Non-CPI Secondary Accession Numbers: 2003-681829